

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 645 473 A1**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **94113518.8**

(51) Int. Cl.<sup>6</sup>: **C23C 22/05**

(22) Date of filing: **30.08.94**

(30) Priority: **31.08.93 JP 215357/93**  
**31.08.93 JP 215358/93**

(43) Date of publication of application:  
**29.03.95 Bulletin 95/13**

(84) Designated Contracting States:  
**DE FR GB**

(71) Applicant: **NIPPON PAINT COMPANY LIMITED**  
**No. 2-1-2, Oyodokita,**  
**Kita-ku**  
**Osaka City,**  
**Osaka (JP)**

(72) Inventor: **Endou, Syunichi**  
**8-22, Hiranohonmachi 5-chome,**  
**Hirano-ku**  
**Osaka-city,**  
**Osaka (JP)**  
Inventor: **Miyamoto, Satoshi**  
**A3-108, 3-6, Shinsenriminamimachi**  
**Toyonaka-city,**  
**Osaka (JP)**  
Inventor: **Yoshida, Yuichi**  
**26-4, Ishiduhigashimachi**  
**Neyagawa-city,**  
**Osaka (JP)**

(74) Representative: **TER MEER - MÜLLER -**  
**STEINMEISTER & PARTNER**  
**Mauerkircherstrasse 45**  
**D-81679 München (DE)**

(54) **Chemical conversion method and surface treatment method for metal can.**

(57) Quaternary ammonium salt having at least one alkyl group of 10 to 20 in carbon number is added to a chemical conversion solution to be at least 20 ppm in concentration, and a chemical conversion coating is formed on a surface of a metal can with this chemical conversion solution. After the chemical conversion coating is formed on the surface of the metal can with the chemical conversion solution, a surface treatment solution containing quaternary ammonium salt having at least one alkyl group of 10 to 20 in carbon number is applied to the surface of the metal can provided with the chemical conversion coating.

**EP 0 645 473 A1**

## BACKGROUND OF THE INVENTION

## Field of the Invention

- 6 The present invention relates to a chemical conversion method of forming a chemical conversion coating on the surface of a metal can with a chemical conversion solution, and a surface treatment method for a metal can.

## Description of the Background Art

- 10 Metal cans include a two-piece can consisting of a bottomed cylindrical barrel and a top plate, and a three-piece can consisting of a bottomless cylindrical barrel, a base plate and a top plate. The barrels of such metal cans are generally formed by metal plates, which are successively treated in order of preliminary degreasing, degreasing, rinsing, chemical conversion, rinsing, drying and coating after forming.
- 15 A number of can barrels are carried along a laterally wide line at a high speed and subjected to, treatment through the forming step to the drying step, while the width of the line is reduced between the drying step and the coating step so that the can barrels as gathered are carried one by one along the narrowed line. In the coating step, the can barrels which are carried one by one are successively subjected to printing or coating on the outer surfaces thereof.
- 20 When the width of the line is reduced as described above, the can barrels as gathered come into contact or collide with each other. Particularly when barrels of aluminum cans having high surface roughness and a high friction coefficient in general are carried at an extremely high speed and gathered together, mobility thereof is so deteriorated that the can barrels are collapsed or broken due to mutual contact or collision, or sprung out from the conveyor.
- 25 Japanese Patent Laying-Open No. 64-85292 (1989) discloses a technique of employing a water-soluble material such as ethylene oxide addition alcohol phosphate, ethylene oxide addition alcohol or ethylene oxide addition fatty acid as a surface treatment agent, applying the same to the outer surfaces of metal cans by spraying or the like for reducing the friction coefficients of the outer surfaces, thereby improving mobility of the cans.
- 30 On the other hand, each of Japanese Patent Laying-Open Nos. 3-207766 (1991) and 4-66671 (1992) discloses a technique of employing a surface treatment solution of pH 4 to 6 consisting of polystyrene resin, orthophosphoric acid or condensed phosphoric acid and water and applying the same to the surfaces of can barrels thereby improving sliding quality of the same.
- However, the ethylene oxide adduct of fatty acid disclosed in Japanese Patent Laying-Open No. 64-  
35 85292 is water-soluble and hence this surface-treatment solution is disadvantageously removed when the can barrels are rinsed after application thereof. Therefore, this surface treatment solution is introduced into water which is employed in the final rinsing step. Thus, the can barrels cannot be completely rinsed and water tends to remain in bottoms or flange portions of the can barrels to leave the component of the surface treatment agent in a condensed state, leading to reduction in film adhesion.
- 40 Further, a conveyor for carrying the can barrels cannot be completely rinsed either and hence the same is disadvantageously contaminated by the component of the surface treatment agent adhering thereto.
- Further, the surfaces of the cans may have strong water repellency depending on the component of the surface treatment agent, leading to difficulty in handling in later steps.
- The ethylene oxide addition alcohol phosphate disclosed in the aforementioned gazette is not completely removed by rinsing but maintains sliding quality due to its adsorptivity to the chemical conversion  
45 coatings provided on the surfaces of the metal cans, although the same is water-soluble. However, this surface treatment agent is extremely inferior in film adhesion.
- On the other hand, the method disclosed in Japanese Patent Laying-Open No. 3-207766 etc. employs a solution containing resin and therefore requires a specific step in addition to general steps, leading to  
50 complicated manufacturing steps. Further, aluminum cans are disadvantageously nigrified when the same are heated by boiling water after coating, leading to inferiority in resistance against the so-called boiling water nigrification.

## SUMMARY OF THE INVENTION

- 55 An object of the present invention is to provide a chemical conversion method and a surface treatment method for a metal can, which can provide excellent sliding quality to the outer surface of a metal can, and neither reduction of the sliding quality nor reduction of the film adhesion is caused by rinsing.

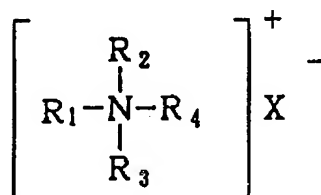
A chemical conversion method according to a first aspect of the present invention comprises the steps of adding quaternary ammonium salt having at least one alkyl group of 10 to 20 in carbon number to a chemical conversion solution to be at least 20 ppm in concentration, and forming a chemical conversion coating on the surface of a metal can with the chemical conversion solution.

6 A surface treatment method according to a second aspect of the present invention comprises the steps of forming a chemical conversion coating on the surface of a metal can with a chemical conversion solution, and coating the surface of the metal can, which is provided with the chemical conversion coating, with a surface treatment solution containing quaternary ammonium salt having at least one alkyl group of 10 to 20 in carbon number.

10 The quaternary ammonium salt employed in each of the first and second aspects of the present invention is not particularly restricted so far as the same has at least one alkyl group of 10 to 20 in carbon number, while this ammonium salt can be prepared from a compound which is expressed in the following formula, for example:

15

20



25 where each of  $R_1$  to  $R_4$  represents an alkyl group, an alkoxy group or a benzyl group of 1 to 20 in carbon number with at least one of these symbols representing an alkyl group 10 to 20 in carbon number, and X represents Cl,  $SO_4$ ,  $NO_3$  or F.

The quaternary ammonium salt employed in each of the first and second aspects of the present invention is preferably about 150 to 800 in molecular weight.

30 In the first aspect of the present invention, the quaternary ammonium salt is added to the chemical conversion solution in such an amount that the same is at least 20 ppm in concentration. If the concentration of the quaternary ammonium salt is less than 20 ppm, it is impossible to attain a sufficient effect of reducing the friction coefficient of the metal can. Further, the amount of the quaternary ammonium salt is preferably not more than 1000 ppm. If the amount exceeds 1000 ppm, the metal can may be badly influenced in appearance and quality after drying. The amount of the quaternary ammonium salt is more preferably 50 to 800 ppm, and further preferably 100 to 500 ppm.

The chemical conversion solution to which the quaternary ammonium salt is added in the first aspect of the present invention can be prepared from a generally known one, such as chemical conversion solutions which can form chemical conversion coatings of phosphate and/or fluorine compounds, for example.

40 Concentration of the quaternary ammonium salt contained in the surface treatment solution which is employed in the second aspect of the present invention is not particularly restricted but appropriately adjusted in response to the method of applying the surface treatment solution. When the surface treatment solution is applied to the surface of the metal can by a general spraying method, the concentration of the quaternary ammonium salt is preferably about 20 to 1000 ppm. If the concentration is less than 20 ppm, it may not be possible to make the surface of the metal can adsorb a sufficient amount of the quaternary ammonium salt. If the surface treatment solution is applied in high concentration exceeding 1000 ppm, on the other hand, the quaternary ammonium salt is adsorbed in such an excess amount that the same may be removed in rinsing or the like, or exert a bad influence on the appearance and quality of the metal can. The concentration of the quaternary ammonium salt is more preferably 50 to 800 ppm, and further preferably 100 to 500 ppm.

50 The chemical treatment solution employed in the second aspect of the present invention can be prepared from a generally known one, such as chemical treatment solutions which can form chemical conversion coatings of phosphate and/or fluorine compounds, for example.

55 In each of the first and second aspects of the present invention, the chemical treatment solution preferably contains at least 10 ppm of phosphoric acid ions and/or fluorine ions or complex fluoride ions, and at least 10 ppm of transition metal ions in composition. The transition metal ions can be prepared from zirconium, titanium, hafnium, vanadium and/or cerium. The transition metal ions may be contained as metal cations and complex ions. The content of the phosphoric acid ions and/or fluorine ions or complex fluoride

ions is further preferably 10 to 1000 ppm in the chemical treatment solution. The complex fluoride ions can be prepared from silicofluoride ions or borofluoride ions. Both of the fluoride ions and the complex fluorid ions may be contained in the chemical conversion solution. A further preferable content of the transition metal ions of zirconium or the like is 20 to 125 ppm.

5 In the first aspect of the present invention, the chemical conversion treatment may be carried out a plurality of times. For example, a chemical conversion coating may be formed with a chemical conversion solution containing no quaternary ammonium salt, so that the chemical conversion coating is thereafter subjected to chemical conversion treatment with a chemical conversion solution containing quaternary ammonium salt. It is possible to further improve boiling water nigrification resistance by forming the  
10 chemical conversion coating with the chemical conversion solution containing no quaternary ammonium salt as an underlayer coating.

In the first aspect of the present invention, a defoaming agent may be added to the chemical treatment solution at need. Also in the second aspect of the present invention, a defoaming agent may be added to the chemical treatment solution at need. In particular, quaternary ammonium salt having a substitutional  
15 group to which ethylene oxide is added tends to cause a problem of foaming, and hence about 0.5 to 3 percent by weight of a defoaming agent may be added to this quaternary ammonium salt. Such a defoaming agent can be prepared from a nonionic surface active agent such as Pluronic type alcohol ethylene oxide propylene oxide adducts, sorbitan fatty acid esters or the like.

According to the first aspect of the present invention, it is possible to form an inorganic-organic  
20 composite film comprising a chemical conversion coating which adsorbs quaternary ammonium salt, by adding specific quaternary ammonium salt to a chemical treatment solution and carrying out chemical conversion treatment. The quaternary ammonium salt is so strongly adsorbed by the chemical conversion coating that the same is not removed when the coating is rinsed after the chemical conversion treatment but maintains an effect for serving as lubricant, whereby the treated surface has sliding quality after the  
25 rinsing. Further, the sliding quality is still maintained after later treatment such as acid rinsing.

According to the first aspect of the present invention, therefore, it is possible to provide excellent sliding quality so that the coating is not removed by rinsing, thereby improving mobility of the metal can. Further, it is possible to smoothly introduce/take out a mandrel into/from the can barrel for making printing/coating on the metal can, thereby reducing wear of the mandrel.

30 Further, the chemical conversion coating which is formed according to the first aspect of the present invention has excellent film adhesion.

In addition, the chemical conversion coating which is formed according to the first aspect of the present invention exhibits no water repellency but provides excellent wettability in rinsing, leading to easy handling in later steps.

35 According to the second aspect of the present invention, a surface treatment solution containing specific quaternary ammonium salt is applied to the surface of a metal can which is provided with a chemical conversion coating, so that the quaternary ammonium salt is adsorbed by the chemical conversion coating.

The quaternary ammonium salt is so strongly adsorbed by the chemical conversion coating that the  
40 same is not removed upon rinsing after the surface treatment but maintains an effect for serving as lubricant, whereby the treated surface has sliding quality after the rinsing. Further, the sliding quality is still maintained after later treatment such as acid rinsing.

According to the second aspect of the present invention, therefore, it is possible to provide excellent sliding quality to the coating so that the same is not removed by rinsing, thereby improving mobility of the metal can. Further, it is possible to smoothly introduce/take out a mandrel into/from the can barrel for making printing/coating on the metal can, thereby reducing wear of the mandrel.

In addition, the metal can which is surface-treated according to the second aspect of the present invention has excellent film adhesion. The reason why the surface treatment method according to the second aspect of the present invention provides excellent film adhesion is not yet clarified in detail, but the  
50 excellent film adhesion may conceivably result from affinity to a film which is formed thereon.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention.

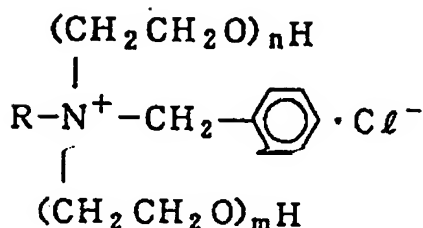
#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

55

The first aspect of the present invention is now described with reference to Examples, while the first aspect is not restricted to the following Examples.

Example 1

The following beef tallow amine ethylene oxide adduct benzyl chloride was employed as quaternary ammonium salt:



where R represents beef tallow, and n and m represent integers of 1 to 2.

The surface of a barrel of metal can which was prepared by forming an aluminum plate was treated through steps of degreasing, rinsing 1, chemical conversion, rinsing 2, pure water rinsing and drying.

The respective steps are now described.

(Degreasing)

A 3.5 wt.% aqueous solution which was prepared by dissolving a degreasing agent (Surf Cleaner NHC-100 (trade name): concentrated degreasing solution by Nippon Paint Co., Ltd.) in water was sprayed onto the aluminum can barrel at 60 °C for 2 minutes.

(Rinsing 1)

Industrial water was sprayed onto the degreased can barrel at the room temperature for 10 seconds.

(Chemical Conversion)

A solution, which was prepared by adding a 5 wt.% aqueous solution of the surface treatment agent expressed in the aforementioned chemical formula to a 2.5 wt.% aqueous solution which was prepared by dissolving a phosphate treatment solution (Alsurf 4040 (trade name): zirconium phosphate treatment agent by Nippon Paint Co., Ltd.) in water and adjusting the same to pH 3.0 with aqueous ammonia so that quaternary ammonium salt was 20 ppm, was sprayed onto the can barrel, which was rinsed in the rinsing 1 step, at 40 °C for 20 seconds.

(Rinsing 2)

Industrial water was sprayed onto the chemically converted can barrel at the room temperature for 10 seconds.

(Pure Water Rinsing)

Pure water was sprayed onto the can barrel, which was subjected to the rinsing 2 step, at the room temperature for 10 seconds.

(Drying)

The can barrel, which was subjected to the pure water rinsing step, was dried at 200 °C for 2 minutes.

Example 2

A metal can was treated similarly to Example 1, except that quaternary ammonium salt was added to be 100 ppm in the chemical conversion step.

Example 3

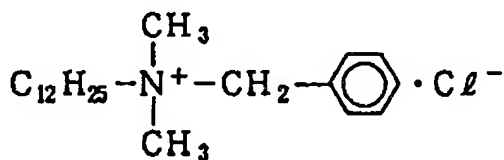
A metal can was treated similarly to Example 1, except that quaternary ammonium salt was added to be 500 ppm in the chemical conversion step.

Example 4

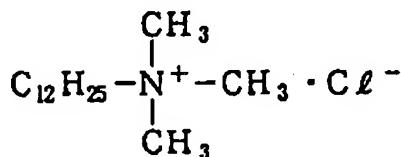
A metal can was treated similarly to Example 1, except that quaternary ammonium salt was added to be 1000 ppm in the chemical conversion step.

Example 5

A metal can was treated similarly to Example 1, except that the following lauryl dimethylamine benzyl chloride was employed as quaternary ammonium salt to be added to the chemical conversion solution in the chemical conversion step and this quaternary ammonium salt was added to be 500 ppm.

Example 6

A metal can was treated similarly to Example 1, except that the following lauryl trimethylammonium chloride was employed as quaternary ammonium salt to be added to the chemical conversion solution in the chemical conversion step and this quaternary ammonium salt was added to be 500 ppm.

Comparative Example 1

A metal can was treated similarly to Example 1, except that no quaternary ammonium salt was added to the chemical conversion solution in the chemical conversion step.

Comparative Example 2

A metal can was treated similarly to Example 1, except that no quaternary ammonium salt was added to the chemical conversion solution but an isostearic acid ethylene oxide adduct (Ethox MI-14 (trade name) by Ethox Co., Ltd.) was added to be 500 ppm in the chemical conversion step.

Comparative Example 3

A metal can was treated similarly to Example 1, except that no quaternary ammonium salt was added to the chemical conversion solution but an ester phosphate ethylene oxide adduct (Gafac PE510 (trade name) by Phone-Poulenc/GAF) was added to be 500 ppm in the chemical conversion step.

The metal cans of Examples 1 to 6 and comparative examples 1 to 3 obtained in the aforementioned manners were subjected to valuation of friction coefficients, states after rinsing and adhesion values after coating.

The friction coefficients were measured by a Haydon rubbing tester (with a load of 250 g and roller fixation of 100 mm/min.).

The adhesion values after coating were evaluated on coatings which were formed by applying epoxyacrylic paints by a bar coater to be 4  $\mu\text{m}$  in thickness and drying the same in atmosphere of 250 °C for 30 seconds. Primary adhesion was evaluated by a 1 mm cross-cut adhesion test after coating. Secondary adhesion was evaluated by a 1 mm cross-cut adhesion test after dipping samples in boiling water for 30 minutes.

The states after rinsing were visually observed.

Table 1 shows the results of measurement.

Table 1

15

	Concentration (ppm)	Friction Coefficient	State after Rinsing	Adhesion after Coating	
				Primary	Secondary
Example 1	20	0.80	Wettable	100/100	100/100
Example 2	100	0.41	Wettable	100/100	100/100
Example 3	500	0.21	Wettable	100/100	100/100
Example 4	1000	0.22	Wettable Partially Water-Repellent	100/100	100/100
Example 5	500	0.30	Wettable	100/100	100/100
Example 6	500	0.43	Wettable	100/100	100/100
Comparative Example 1	0	0.89	Wettable	100/100	100/100
Comparative Example 2	500	0.88	Wettable	100/100	100/100
Comparative Example 3	500	0.28	Water-Repellent	0/100	0/100

35

It is clearly understood from Table 1 that the metal cans of Examples 1 to 6 according to the first aspect of the present invention exhibit low friction coefficients, with excellent sliding quality. It is also understood that these metal cans can be surface-treated in states having low water repellency also after rinsing. Further, the metal cans surface-treated according to the first aspect of the present invention have excellent film adhesion, as clearly understood from the results of adhesion after coating.

Description is now made on Examples of carrying out chemical conversion treatment twice for adding quaternary ammonium salt in the second chemical conversion treatment.

#### Example 7

45

A can barrel of a metal can obtained by forming an aluminum plate was continuously carried so that its surface was treated through steps of degreasing, rinsing 1, chemical conversion 1, chemical conversion 2, rinsing 2, pure water rinsing and drying.

The degreasing, rinsing 1, rinsing 2, pure water rinsing and drying steps were carried out similarly to those of Example 1. The chemical conversion 2 step was also carried out by adding quaternary ammonium salt to be 20 ppm, similarly to the chemical conversion step of Example 1. In the chemical conversion 1 step, chemical conversion was carried out with a chemical conversion solution containing no quaternary ammonium salt, similarly to conventional treatment.

(Chemical Conversion 1)

A 2.5 wt.% aqueous solution, which was prepared by dissolving a phosphate treatment solution (Alsurf 4040 (trade name)) in water and adjusting the same to pH 3.0 with aqueous ammonia, was sprayed onto the

can barrel at 40 °C for 20 seconds.

#### Example 8

- 6 A metal can was treated similarly to Example 7, except that quaternary ammonium salt was added to be 100 ppm in the chemical conversion 2 step.

#### Example 9

- 10 A metal can was treated similarly to Example 7, except that quaternary ammonium salt was added to be 500 ppm in the chemical conversion 2 step.

#### Example 10

- 15 A metal can was treated similarly to Example 7, except that quaternary ammonium salt was added to be 1000 ppm in the chemical conversion 2 step.

#### Comparative Example 4

- 20 A metal can was treated similarly to Example 7, except that no quaternary ammonium salt was added to the chemical conversion solution but an isostearic acid ethylene oxide adduct (Ethox MI-14 (trade name) by Ethox Co., Ltd.) was added to be 500 ppm.

#### Comparative Example 5

- 25 A metal can was treated similarly to Example 7, except that no quaternary ammonium salt was added to the chemical conversion solution but a phosphoric acid ester ethylene oxide adduct (Gafac PE510 (trade name) by Phone-Poulenc/GAF) was added to be 500 ppm.

- 30 The metal cans of Examples 7 to 10 and comparative examples 4 and 5 obtained in the aforementioned manners were subjected to evaluation of friction coefficients, states after rinsing and adhesion values after coating, similarly to Examples 1 to 6. Table 2 shows the results.

Table 2

	Concentration (ppm)	Friction Coefficient	State after Rinsing	Adhesion after Coating	
				Primary	Secondary
35 Example 7	20	0.58	Wettable	100/100	100/100
40 Example 8	100	0.30	Wettable	100/100	100/100
Example 9	500	0.21	Wettable	100/100	100/100
Example 10	1000	0.20	Frang Partially Water-Repellent	100/100	100/100
45 Comparative Example 4	500	0.86	Wettable	100/100	100/100
Comparative Example 5	500	0.27	Water-Repellent	0/100	0/100

- 50 It is clearly understood from Table 1 that the metal cans of Examples 7 to 10 which were chemically converted according to the first aspect of the present invention exhibit low friction coefficients with excellent sliding quality as well as excellent adhesion after coating.

The second aspect of the present invention is now described with reference to Examples, while the second aspect is not restricted to the following Examples.

#### 55 Example 11

The same beef tallow amine ethylene oxide adduct benzyl chloride as that employed in Example 1 was used as quaternary ammonium salt.



The surface of a can barrel of a metal can which was prepared by forming an aluminum plate was treated through steps of degreasing, rinsing 1, chemical conversion, surface treatment, rinsing 2, pure water rinsing and drying.

The respective steps are now described.

5

(Degreasing)

A 3.5 wt.% aqueous solution which was prepared by dissolving a degreasing agent (Surf Cleaner NHC-100 (trade name); concentrated degreasing solution by Nippon Paint Co., Ltd.) in water was sprayed onto the aluminum can barrel at 60 °C for 2 minutes.

10

(Rinsing 1)

Industrial water was sprayed onto the degreased can barrel at the room temperature for 10 seconds.

15

(Chemical Conversion)

A 2.5 wt.% aqueous solution, which was prepared by dissolving a phosphate treatment solution (Alsurf 4040 (trade name); zirconium phosphate treatment agent by Nippon Paint Co., Ltd.) in water and adjusting the same to pH 3.0 with aqueous ammonia, was sprayed onto the can barrel, which was rinsed in the rinsing 1 step, at 40 °C for 20 seconds.

20

(Surface Treatment)

A 1 wt.% aqueous solution of the aforementioned quaternary ammonium salt was sprayed onto the can barrel at the room temperature for 20 seconds.

25

(Rinsing 2)

Industrial water was sprayed onto the chemically converted can barrel at the room temperature for 10 seconds.

30

(Pure Water Rinsing)

Pure water was sprayed onto the can barrel, which was subjected to the rinsing 2 step, at the room temperature for 10 seconds.

35

(Drying)

The can barrel, which was subjected to the pure water rinsing step, was dried at 200 °C for 2 minutes.

40

#### Example 12

A metal can was treated similarly to Example 11, except that the lauryl dimethylamine benzyl chloride employed in Example 5 was used as quaternary ammonium salt to be added in the surface treatment step.

45

#### Example 13

A metal can was treated similarly to Example 11, except that the lauryl trimethylammonium chloride employed in Example 6 was used as quaternary ammonium salt to be added in the surface treatment step.

50

#### Comparative Example 6

A metal can was treated similarly to Example 11, except that no surface treatment was made but the rinsing 2 step was carried out immediately after the chemical conversion step.

55

Comparative Example 7

A metal can was treated similarly to Example 11, except that a 1 wt.% aqueous solution of an isostearic acid ethylene oxide adduct (Ethox MI-14 (trade name) by Ethox Co., Ltd.) was employed in place of quaternary ammonium salt in the surface treatment step.

Comparative Example 8

A metal can was treated similarly to Example 11, except that a 1 wt.% aqueous solution of an ester phosphate ethylene oxide adduct (Gafac PE510 (trade name) by Phone-Poulenc/GAF) was employed in place of quaternary ammonium salt in the surface treatment step.

The metal cans of Examples 11 to 13 and comparative examples 6 to 8 obtained in the aforementioned manners were subjected to evaluation of friction coefficients, states after rinsing and adhesion values after coating.

The friction coefficients were measured by a Haydon rubbing tester (with a load of 250 g and roller fixation of 100 mm/min.).

Adhesion values after coating were evaluated on coatings which were formed by applying epoxyacrylic paints by a bar coater to be 4 µm in thickness and drying the same in atmosphere of 250°C for 30 seconds. Primary adhesion was evaluated by a 1 mm cross-cut adhesion test after coating. Secondary adhesion was evaluated by a 1 mm cross-cut adhesion test after dipping samples in boiling water for 30 minutes.

The states after rinsing were visually observed.

Table 3 shows the results of measurement.

Table 3

	Friction Coefficient	Adhesion After Coating	
		Primary	Secondary
Example 11	0.21	100/100	100/100
Example 12	0.30	100/100	100/100
Example 13	0.43	100/100	100/100
Comparative Example 6	0.88	100/100	100/100
Comparative Example 7	0.87	100/100	100/100
Comparative Example 8	0.28	0/100	0/100

It is clearly understood from Table 3 that the metal cans of Examples 11 to 13 according to the second aspect of the present invention exhibit low friction coefficients, with excellent sliding quality. Further, the metal cans which were surface-treated according to the second aspect of the present invention have excellent film adhesion, as clearly understood from the results of adhesion after coating.

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

**Claims**

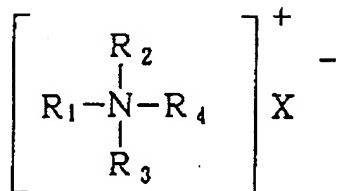
1. A chemical conversion method for forming a chemical conversion coating on a surface of a metal can with a chemical conversion solution, said method comprising the steps of:  
 adding quaternary ammonium salt having at least one alkyl group of 10 to 20 in carbon number to said chemical conversion solution to be at least 20 ppm in concentration; and  
 chemically converting said surface of said metal can with said chemical conversion solution.
2. A chemical conversion method in accordance with claim 1, wherein said chemical conversion solution contains at least 10 ppm of phosphoric acid ions and/or fluorine ions or complex fluoride ions, and at least 10 ppm of at least one type of metal ions selected from the group consisting of zirconium,

titanium, hafnium, vanadium and cerium.

3. A chemical conversion method in accordance with claim 1, wherein said quaternary ammonium salt is a compound being expressed in the following formula:

5

10



15

where each of  $R_1$  to  $R_4$  represents an alkyl group, an alkoxy group or a benzyl group of 1 to 20 in carbon number, at least one of these symbols representing an alkyl group of 10 to 20 in carbon number, and X represents Cl,  $SO_4$ ,  $NO_3$  or F.

20

4. A chemical conversion method in accordance with claim 1, wherein the content of said quaternary ammonium salt is 20 to 1000 ppm.

25

5. A chemical conversion method forming a chemical conversion coating on a surface of a metal can with chemical conversion solutions, said method comprising the steps of:

carrying out first chemical conversion treatment with a first chemical conversion solution;

adding quaternary ammonium salt having at least one alkyl group of 10 to 20 in carbon number to a second chemical conversion solution to be at least 20 ppm in concentration; and

carrying out second chemical conversion treatment with said second chemical conversion solution.

30

6. A chemical conversion solution for a metal can containing:

at least 10 ppm of phosphoric acid ions and/or complex fluoride ions;

at least 10 ppm of at least one type of metal ions being selected from the group consisting of zirconium, titanium, hafnium, vanadium and cerium; and

at least 20 ppm of quaternary ammonium salt having at least one alkyl group of 10 to 20 in carbon number.

35

7. A surface treatment method for a metal can comprising the steps of:

forming a chemical conversion coating on a surface of said metal can with a chemical conversion solution; and

coating said surface of said metal can being provided with said chemical conversion coating with a surface treatment solution containing quaternary ammonium salt having at least one alkyl group of 10 to 20 in carbon number for surface-treating the same.

40

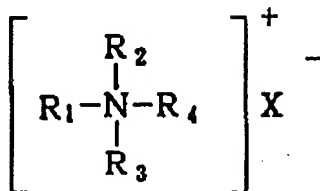
8. A surface treatment method for a metal can in accordance with claim 7, wherein said chemical conversion solution contains at least 10 ppm of phosphoric acid ions and/or fluorine ions or complex fluoride ions, and at least 10 ppm of at least one type of metal ions being selected from the group of zirconium, titanium, hafnium, vanadium and cerium.

45

9. A surface treatment method for a metal can in accordance with claim 7, wherein said quaternary ammonium salt is a compound being expressed in the following formula:

50

55



where each of  $R_1$  to  $R_4$  represents an alkyl group, an alkoxy group or a benzyl group of 1 to 20 in carbon number, at least one of these symbols representing an alkyl group of 10 to 20 in carbon number, and X represents Cl,  $SO_4$ ,  $NO_3$  or F.

10. A surface treatment method for a metal can in accordance with claim 7, wherein the content of said quaternary ammonium salt is 20 to 1000 ppm.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 94113518.8
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 6)
D, A	PATENT ABSTRACTS OF JAPAN, unexamined applications, C section, vol. 16, no. 273, June 18, 1992 THE PATENT OFFICE JAPANESE GOVERNMENT page 31 C 953; & JP-A-04 66 671 (NIPPON PARKERIZING) --	1, 2, 5	C 23 C 22/05
D, A	PATENT ABSTRACTS OF JAPAN, unexamined applications, C section, vol. 15, no. 478, December 4, 1991 THE PATENT OFFICE JAPANESE GOVERNMENT page 127 C 891; & JP-A-03 207 766 (NIPPON PARKERIZING) --	1, 2, 5	
A	DE - A - 3 535 135 (PARKER CHEMICAL) * Claims * -----	1, 2, 5, 8	TECHNICAL FIELDS SEARCHED (Int. Cl. 6)  C 23 C 22/00 C 09 D 5/00
The present search report has been drawn up for all claims			
VIENNA		Date of completion of the search 09-12-1994	Examiner HOPBAUER
<b>CATEGORY OF CITED DOCUMENTS</b>  X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document  T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons  & : member of the same patent family, corresponding document			



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number: **0 659 473 A1**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **94309380.7**

(51) Int. Cl.<sup>8</sup>: **B01J 8/04, C07D 301/12**

(22) Date of filing: **15.12.94**

(30) Priority: **20.12.93 US 171144**  
**22.09.94 US 310546**

(43) Date of publication of application:  
**28.06.95 Bulletin 95/26**

(84) Designated Contracting States:  
**AT BE DE ES FR GB IT NL**

(71) Applicant: **ARCO Chemical Technology, L.P.**  
**Two Greenville Crossing**  
**4001 Kennett Pike, Suite 238**  
**Greenville, Delaware 19807 (US)**

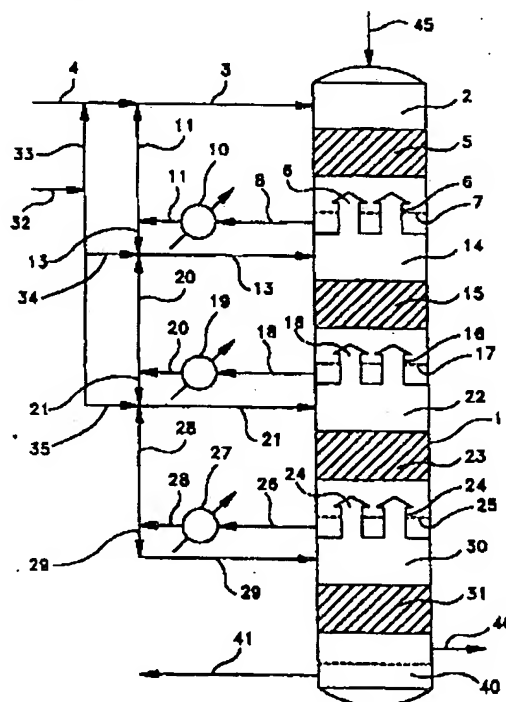
(72) Inventor: **Jubin Jr., John C.**  
**144 Summit House**  
**West Chester PA 19382 (US)**

(74) Representative: **Cropp, John Anthony David et al**  
**MATHYS & SQUIRE**  
**100 Grays Inn Road**  
**London, WC1X 8AL (GB)**

(54) Catalytic converter and method for highly exothermic reactions.

(57) To produce propylene oxide, a reaction liquid comprised of propylene, hydrogen peroxide and propylene oxide and a vapor purge stream is passed through the bed of solid catalyst at reaction conditions in each of a series of catalyst-packed reaction zones (2,14,22,30), the resulting mixture is separated in each zone into a vapor stream which passes to the next reaction zone and a reaction liquid stream (8,18,26), which is removed and cooled to remove exothermic heat of reaction. Some of the cooled liquid (11,20,28) is recycled to the zone from which it was removed and some (13,21,29) is passed to the next in the series of reaction zones. Also provided is a reactor for carrying out the reaction.

FIG-1



EP 0 659 473 A1

The present invention relates to a catalytic converter or reactor and a process for carrying out highly exothermic reactions.

#### Description of the Prior Art

Substantial difficulties are encountered in carrying out highly exothermic reactions where reactants and/or products are temperature sensitive. For example, the catalytic liquid phase reaction of propylene and hydrogen peroxide to produce propylene oxide is a highly exothermic reaction while hydrogen peroxide decomposition is quite temperature sensitive. Thus, removal of the exothermic heat of reaction without causing excess temperature rise presents a serious problem.

Conventional reactors for exothermic reactions are usually of two types:

- (1) Quench type which consist of multiple fixed beds with cold feed quench injected in between beds
- (2) Tubular type in which the catalyst is placed in the tubes of a vertical shell and tube heat exchanger

If the heat of reaction is high, the first type does not provide sufficient heat removal. This can be overcome by recycling cold reactor effluent but this results in the disadvantages associated with back-mixed reactors.

The tubular reactor cost becomes prohibitive when high heats of reaction have to be removed through heat exchanger surfaces operating with a low heat transfer coefficient. There is also a temperature gradient from the center of the tube which is often detrimental to a process which requires nearly isothermal conditions.

U.S. Patents 2,271,848 and 2,322,366 provide catalytic converters for use in catalytic cracking and the like reactions wherein the converters are divided into a series of zones and the reaction mixture from one zone is removed and externally heated or cooled before being returned to the next reaction zone. Such converters are not suitable for the effective temperature and reagent concentration control of a highly exothermic system as is achieved in accordance with the present invention.

#### Brief Description of the Invention

In accordance with the present invention, a catalytic converter tower is provided containing a series of separate zones each having a bed of solid catalyst contained therein. Liquid reaction mixture containing the appropriate reactants is introduced into a zone and passed at reaction conditions through the catalyst bed. The resulting reaction mixture is removed from the reactor and the exothermic heat of reaction is removed by indirect heat exchange. The great bulk of the cooled reaction mixture is recycled to the zone from which it was removed while a smaller portion is passed to the next zone and reacted in a similar fashion.

The recycle of the great bulk of the reaction mixture after cooling insures that only a modest temperature rise takes place in any one reaction zone. The provision of separate reaction zones enables close control of the reaction compositions approaching a plug flow reactor configuration.

#### Description of the Drawing

The accompanying drawings, Figures 1-3, illustrate the improved reactor and various practices of the invention.

#### Detailed Description

Practice of the invention is especially applicable to highly exothermic reactions such as that between propylene and hydrogen peroxide to form propylene oxide. In such a reaction, heat of reaction must be removed and the reaction temperature must be carefully controlled in order to achieve optimum results.

Referring to the attached drawing, Figure 1, a four zone reactor 1 is illustrated. Each of the zones is provided with liquid inlet means near the upper part thereof, a packed bed of solid catalyst particles, liquid withdrawal means near the bottom of each zone, and vapor passage means permitting vapor to pass from one zone to the next; the lowest zone is not provided with the vapor passage means.

As shown in Figure 1 and with reference to the production of propylene oxide by reaction of hydrogen peroxide and propylene, feed propylene and a hydrogen peroxide containing solution as well as recycled cooled reaction mixture containing unreacted propylene and hydrogen peroxide together with product propylene oxide is introduced into zone 2 via line 3. Net hydrogen peroxide feed is introduced into line 3 via line 4. Net propylene is introduced via lines 32 and 33 as liquid. The liquid mixture passes downwardly through packed catalyst bed 5 wherein the exothermic reaction of propylene and hydrogen peroxide to form propylene oxide takes place and there is a modest temperature increase of the mixture as a result of the reaction exotherm.

The reaction mixture passes through catalyst bed 5 into the lower section of zone 2. Risers 6 are provided permitting vapor passage downwardly to the next lower zone but preventing passage of liquid therethrough. Liquid level 7 is maintained in the lower section of zone 2 by known liquid level control means.

Liquid reaction mixture is withdrawn from zone 2 via line 8 and passes to indirect heat exchanger 10 wherein the reaction exotherm is removed and the circulating mixture is cooled to about its original temperature.

Most of the cooled mixture passes via lines 11 and 13 back to zone 2 together with the net propylene and hydrogen peroxide feed.

A minor portion of the cooled reaction mixture from zone 2 passes from cooler 10 via lines 11 and 13 to reaction zone 14 in combination with cooled recycle liquid from zone 14 and additional net liquid propylene added via lines 32 and 34.

Zone 14 is essentially similar to zone 2 with the reaction liquid passing downwardly through packed catalyst bed 15 wherein further reaction of hydrogen peroxide with propylene takes place. Risers 16 permit vapor passage therethrough and liquid level 17 is maintained in the lower section of zone 14.

Reaction liquid passes from zone 14 via line 18, to heat exchanger 19 where the reaction exotherm generated in zone 14 is removed. Most of the liquid cooled in exchanger 19 passes via lines 20 and 21 back to zone 14. A minor portion passes via lines 20 and 21 to the next reaction zone 22 together with recycled reaction mixture from zone 22 and additional net liquid propylene introduced via lines 32 and 35.

Zone 22 is similar to the preceding zones. The reaction mixture is passed downwardly through catalyst bed 23 wherein further exothermic reaction of propylene and hydrogen peroxide takes place. Risers 24 permit vapor passage therethrough and liquid level 25 is maintained in the lower section of zone 22.

Reaction liquid passes from zone 22 via line 26 to heat exchanger 27 where the reaction exotherm generated in zone 22 is removed. Most of the cooled liquid passes from exchanger via lines 28 and 29 back to zone 22. A minor portion passes via lines 28 and 29 to the next reaction zone 30.

Zone 30 is similar to the preceding zones but being the bottom zone has no risers for vapor passage. The reaction mixture passes downwardly through bed 31 of packed catalyst wherein the reaction between propylene and hydrogen peroxide is completed. Product liquid is removed via line 41. The lowest reaction zone is essentially a zone where the last generally small amount of hydrogen peroxide is reacted. Normally there is not sufficient reaction exotherm to warrant cooling and partial recycle of the liquid removed therefrom.

In the reactor illustrated in Figure 1, zone 30 is the lowest and last reaction zone although it will be apparent that a greater or lesser number of zones can be utilized.

A small amount of propylene vapor is introduced into zone 2 via line 45 for purposes of purging any oxygen formed by hydrogen peroxide decomposition. Vapor passes through each zone through catalyst beds 5, 15, 23, and 31 via risers 6, 16, and 24 and is removed as a purge stream via line 46.

There are several advantages which are achieved through practice of the invention. By circulating large quantities of reaction liquid, temperature increase in any one zone can be kept quite small. Due to removal of the exothermic heat by cooling the liquid from each zone, close control of the reaction conditions can be achieved. By maintaining the plurality of separate zones, plug flow reactor conditions are approached and the benefits of reduced product concentrations in the earlier zones are achieved.

In general, of the liquid reaction mixture removed from each zone of the reactor, 60 to 90% is recycled after cooling with 10 to 40% moving forward to the next zone. Generally, flow in each zone is maintained at a level sufficient to limit the temperature rise in a zone to about 10 to 30°C, preferably 5 to 15°C.

A feature of the production of propylene oxide by the present invention is that the selectivity and yields of the desired propylene oxide product are improved by maintaining lower concentrations of hydrogen peroxide and product propylene oxide in the reaction mixture. This can be readily accomplished by dividing the net hydrogen peroxide feed among the several reaction zones rather than feeding all of the net hydrogen peroxide to the first zone or by adding substantial quantities of a diluent such as isopropanol, methanol or mixtures to the first reaction zone or by a combination of these procedures.

Figure 2 illustrates a practice of the invention which is analogous to that shown in Figure 1 except that the net hydrogen peroxide feed is divided and fed equally to the several reaction zones.

Figure 3 illustrates a practice of the invention which is analogous to that shown in Figure 1 except that alcohol diluent is added to the first reaction zone.

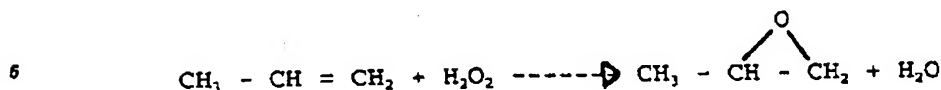
With reference to Figure 2, the system described therein is essentially similar to that of Figure 1 except that instead of all of the net hydrogen peroxide feed passing via lines 4 and 3 to zone 2, the net hydrogen peroxide feed is split and fed in equal amounts to zones 202, 214 and 222 via lines 204A, 204B and 204C respectively.

With reference to Figure 3, the system described therein is essentially similar to that of Figure 2 except that a diluent alcohol stream is added to zone 302 via lines 304D and 303.

The following examples illustrate the invention. In these examples, propylene oxide is produced by the



liquid phase reaction of propylene and hydrogen peroxide in accordance with the following reaction:



Solid titanium silicalite is employed as catalyst; see U.S. Patent 5,214,168.

#### 10 Example 1

Referring to Figure 1, net feed of hydrogen peroxide in isopropanol/water solvent is introduced via line 4 and line 3 to zone 2 with 14 mols/hr. propylene introduced via lines 32 and 33 in combination with 800 mols/hr of recycled reaction mixture via line 11. The total feed to zone 2 comprises 9.2 mol% propylene, 7.4 mol% hydrogen peroxide, mol% propylene oxide, 48.3 mol% isopropanol, and 32 mol% water. The liquid stream entering zone 2 is at 50°C. Purge propylene vapor is introduced into zone 2 via line 45 at the rate of 1 mol/hr.

The liquid passes through catalyst bed 5 wherein propylene and hydrogen peroxide react in accordance with the above equation. The liquid temperature is increased to 58°C as a result of the reaction exotherm.

The liquid reaction mixture comprised of 8.8 mol% propylene, 7 mol% hydrogen peroxide, 3.5 mol% propylene oxide, 48.2 mol% isopropanol, and 32.5 mol% water passes at the rate of 914 mols/hr from zone 2 via line 8 and is cooled to 50°C in exchanger 10.

About 800 mols/hr of the cooled mixture is recycled via lines 11 and 3 to zone 2. About 114 mols/hr of the cooled liquid passes via lines 11 and 13 to the next reaction zone 14 together with 800 mols/hr of cooled recycle reaction liquid via line 20 and 4 mols/hr. liquid propylene via lines 32 and 34. The total liquid feed to zone 14 comprises 8.9 mol% propylene, 3.9 mol% hydrogen peroxide, 6.3 mol% propylene oxide, 46.6 mol% isopropanol, and 34.3 mol% water. Temperature of the liquid introduced to zone 14 is 50°C.

In zone 14, the reaction liquid passes through catalyst bed 15 where further reaction in accordance with the above equation takes place. Liquid temperature increases to 58°C as a result of the reaction exotherm.

Reaction liquid passes from zone 14 via line 18 to exchanger 19 at the rate of 918 mols/hr. This liquid comprises 8.5 mol% propylene, 3.5 mol% hydrogen peroxide, 6.7 mol% propylene oxide, 46.5 mol% isopropanol, and 34.8 mol% water. The liquid is cooled to 50°C in exchanger 19.

About 800 mols/hr of the cooled mixture is recycled via lines 20 and 13 to zone 14. About 118 mols/hr of the cooled liquid passes via lines 20 and 21 to the next reaction zone 22 together with 800 mols/hr of cooled recycle reaction liquid via line 28 and 4 mols/hr. liquid propylene via lines 32 and 35. The total liquid to zone 22 comprises 8.7 mol% propylene, 0.4 mol% hydrogen peroxide, 9.4 mol% propylene oxide, 45.1 mol% isopropanol, and 36.4 mol% water. Temperature of the liquid introduced to zone 22 is 50°C.

In zone 22, the reaction liquid passes through catalyst bed 23 where further reaction in accordance with the above equation takes place. Liquid temperature increases to 58°C as a result of the reaction exotherm.

Reaction liquid passes from zone 22 via line 26 to exchanger 27 at the rate of 922 mols/hr. This liquid comprises 8.2 mol% propylene, 0 mol% hydrogen peroxide, 9.9 mol% propylene oxide, 45 mol% isopropanol, and 36.9 mol% water. The liquid is cooled to 50°C in exchanger 27.

About 800 mols/hr of the cooled mixture is recycled via lines 28 and 21 to zone 22. About 122 mols/hr. of the cooled liquid passes via lines 28 and 29 to the last reaction zone 30.

In zone 30, the reaction liquid passes through catalyst bed 31 where the remaining small reaction takes place. Liquid temperature increase is small, less than 8°C as a result of the reaction exotherm and about 122 mols/hr. of liquid product is recovered via line 41.

Purge vapor in amount of 1.2 mols/hr. is removed via line 46 and comprises 84 mol% propylene, 8 mol% water and isopropanol, and 8 mol% oxygen.

The overall yield of propylene oxide based on hydrogen peroxide is 90%. This compares with a yield of about 80% which is achieved using conventional tubular reactors wherein the temperature rise in the catalyst exceeds 15°C.

#### Example 2

Referring to Figure 2, net feed of hydrogen peroxide in isopropanol/water solvent is introduced at the rate of 100 mols/hr via line 204. The feed composition comprises 33 mol% water, 55 mol% isopropanol and 12 mol% hydrogen peroxide. This net hydrogen peroxide feed is divided with 34 mols/hr passing via line 204A and 203 to zone 202, 33 mols/hr passing via lines 204B, 220 and 213 to zone 214, and 33 mols/hr passing via lines

204C, 228 and 221 to zone 222.

The 34 mols/hr of hydrogen peroxide feed is combined with feed propylene introduced via line 232 and with recycle reaction mixture via line 211 to form a feed mixture to zone 202 via line 203 of 861 mols/hr comprised of 241 mols/hr water, 331 mols/hr isopropanol, 18 mols/hr hydrogen peroxide, 228 mols/hr propylene and 41 mols/hr propylene oxide. This mixture is fed to zone 202 at 54.4°C and 240 psia.

The liquid passes through catalyst bed 205 wherein propylene and hydrogen peroxide react in accordance with the above equation. The liquid temperature is increased to 60°C as a result of the reaction exotherm.

The liquid reaction mixture comprised of 25.1 mol% propylene, 1.68 mol% hydrogen peroxide, 6.17 mol% propylene oxide, 38.9 mol% isopropanol, and 28.7 mol% water passes at the rate of 849 mols/hr from zone 202 via line 208 and is cooled to 54.4°C in exchanger 10.

About 800 mols/hr of the cooled mixture is recycled via lines 211 and 203 to zone 202. About 49 mols/hr of the cooled liquid passes via lines 211 and 213 to the next reaction zone 214 together with 800 mols/hr of cooled recycle reaction liquid via line 220, 25 mols/hr liquid propylene via lines 232 and 234, and 33 mols/hr of the hydrogen peroxide feed. The total liquid feed to zone 214 comprises 26.1 mol% propylene, 1.82 mol% hydrogen peroxide, 5.5 mol% propylene oxide, 37.8 mol% isopropanol, and 28.3 mol% water. Temperature of the liquid introduced to zone 214 is 54.4°C.

In zone 214, the reaction liquid passes through catalyst bed 215 where further reaction in accordance with the above equation takes place. Liquid temperature increases to 60°C as a result of the reaction exotherm.

Reaction liquid passes from zone 214 via line 218 to exchanger 219 at the rate of 896 mols/hr. This liquid comprises 24.9 mol% propylene, 1.45 mol% hydrogen peroxide, 5.9 mol% propylene oxide, 38.3 mol% isopropanol, and 29.1 mol% water. The liquid is cooled to 54.4°C in exchanger 219.

About 800 mols/hr of the cooled mixture is recycled via lines 220 and 213 to zone 214. About 96 mols/hr of the cooled liquid passes via lines 220 and 221 to the next reaction zone 222 together with 800 mols/hr of cooled recycle reaction liquid via line 228, 25 mols/hr liquid propylene via lines 232 and 235, and 33 mols/hr of the hydrogen peroxide feed. The total liquid to zone 222 comprises 26.0 mol% propylene, 1.65 mol% hydrogen peroxide, 6.0 mol% propylene oxide, 37.5 mol% isopropanol, and 28.5 mol% water. Temperature of the liquid introduced to zone 222 is 54.4°C.

In zone 222, the reaction liquid passes through catalyst bed 223 where further reaction in accordance with the above equation takes place. Liquid temperature increases to 60°C as a result of the reaction exotherm.

Reaction liquid passes from zone 222 via line 228 to exchanger 227 at the rate of 943.7 mols/hr. This liquid comprises 24.9 mol% propylene, 1.28 mol% hydrogen peroxide, 6.4 mol% propylene oxide, 37.9 mol% isopropanol, and 29.1 mol% water. The liquid is cooled to 54.4°C in exchanger 227.

About 800 mols/hr of the cooled mixture is recycled via lines 228 and 221 to zone 222. About 143.7 mols/hr of the cooled liquid passes via lines 228 and 219 to the last reaction zone 330.

In zone 230, the reaction liquid passes through catalyst bed 231 where the remaining small reaction takes place. Liquid temperature increase is small, less than 8°C as a result of the reaction exotherm and about 128 mols/hr of liquid product is recovered via line 241.

Purge vapor in amount of 48 mols/hr is removed via line 248 and comprises 82.6 mol% propylene, 0.6 mol% oxygen, 3.8 mol% water and isopropanol, and 3 mol% propylene oxide; this stream is further treated for propylene and propylene oxide recovery (not shown).

The overall yield of propylene oxide based on hydrogen peroxide is 90.8%. This compares with a yield of about 80% which is achieved using conventional tubular reactors wherein the temperature rise in the catalyst exceeds 15°C. The yield is also higher than that is Example 1 due to the separate introduction of hydrogen peroxide feed into the separate zones.

### Example 3

Referring to Figure 3, the net hydrogen peroxide composition and feed rate is the same as for Example 2. The net hydrogen peroxide feed passes at the rate of 34 mols/hr via lines 304A and 303 to zone 302, at the rate of 33 mols/hr via lines 304B and 313 to zone 314, and at the rate of 33 mols/hr via lines 304C, 328 and 321 to zone 322. Isopropanol diluent is fed via lines 304D and 303 to zone 302 at the rate of 100 mols/hr.

The 34 mols/hr of hydrogen peroxide feed and 100 mols/hr of isopropanol are combined with feed propylene introduced via line 332 and with recycle reaction mixture via line 311 to form a feed mixture to zone 302 via line 303 of 808 mols/hr comprised of 54.1 mols/hr water, 484.5 mols/hr isopropanol, 7.1 mols/hr hydrogen peroxide, 271.2 mols/hr propylene and 8.2 mols/hr propylene oxide. This mixture is fed to zone 302 at 54.4°C and 240 psia.

The liquid passes through catalyst bed 305 wherein propylene and hydrogen peroxide react in accordance with the above equation. The liquid temperature is increased to 60°C as a result of the reaction exotherm.

The liquid reaction mixture comprised of 33.3 mol% propylene, 0.5 mol% hydrogen peroxide, 1.35 mol% propylene oxide, 57.6 mol% isopropanol, and 7.1 mol% water passes at the rate of 808 mols/hr from zone 302 via line 308 and is cooled to 54.4°C in exchanger 310.

About 600 mols/hr of the cooled mixture is recycled via lines 311 and 303 to zone 302. About 208 mols/hr of the cooled liquid passes via lines 211 and 213 to the next reaction zone 214 together with 600 mols/hr of cooled recycle reaction liquid via line 220 and 25 mols/hr liquid propylene via lines 332 and 334, and 33 mols/hr of the hydrogen peroxide feed via line 304B. The total liquid feed to zone 314 comprises 34.2 mol% propylene, 1.03 mol% hydrogen peroxide, 1.9 mol% propylene oxide, 52.2 mol% isopropanol, and 10.5 mol% water. Temperature of the liquid introduced to zone 14 is 54.4°C.

In zone 314, the reaction liquid passes through catalyst bed 315 where further reaction in accordance with the above equation takes place. Liquid temperature increases to 60°C as a result of the reaction exotherm.

Reaction liquid passes from zone 314 via line 318 to exchanger 319 at the rate of 860.9 mols/hr. This liquid comprises 33.6 mol% propylene, 0.65 mol% hydrogen peroxide, 2.24 mol% propylene oxide, 52.4 mol% isopropanol, and 10.9 mol% water. The liquid is cooled to 54.4°C in exchanger 319.

About 600 mols/hr of the cooled mixture is recycled via lines 320 and 313 to zone 314. About 280.9 mols/hr of the cooled liquid passes via lines 320 and 321 to the next reaction zone 322 together with 600 mols/hr of cooled recycle reaction liquid via line 328, 25 mols/hr liquid propylene via lines 332 and 335, and 33 mols/hr of the hydrogen peroxide feed via line 304C. The total liquid to zone 322 comprises 33.2 mol% propylene, 1.04 mol% hydrogen peroxide, 2.54 mol% propylene oxide, 49.76 mol% isopropanol, and 13.32 mol% water. Temperature of the liquid introduced to zone 22 is 54.4°C.

In zone 322, the reaction liquid passes through catalyst bed 323 where further reaction in accordance with the above equation takes place. Liquid temperature increases to 60°C as a result of the reaction exotherm.

Reaction liquid passes from zone 322 via line 326 to exchanger 327 at the rate of 908.2 mols/hr. This liquid comprises 32.1 mol% propylene, 0.68 mol% hydrogen peroxide, 2.9 mol% propylene oxide, 50.32 mol% isopropanol, and 13.84 mol% water. The liquid is cooled to 54.4°C in exchanger 327.

About 600 mols/hr of the cooled mixture is recycled via lines 328 and 321 to zone 322. About 308 mols/hr of the cooled liquid passes via lines 328 and 329 to the last reaction zone 330.

In zone 330, the reaction liquid passes through catalyst bed 331 where the remaining small reaction takes place. Liquid temperature increase is small, less than 8°C as a result of the reaction exotherm and about 315 mols/hr. of liquid product is recovered via line 341.

Purge vapor in amount of 5 mols/hr. is removed via line 346 and comprises 92 mol% propylene, 4 mol% water and isopropanol, and 4 mol% oxygen.

The overall yield of propylene oxide based on hydrogen peroxide is 92%. This compares with a yield of about 80% which is achieved using conventional tubular reactors wherein the temperature rise in the catalyst exceeds 15°C. The yield is higher than that for Example 2 due to the lower concentrations of propylene oxide and hydrogen peroxide in the reaction zones.

## Claims

1. A continuous process for the exothermic reaction of propylene and hydrogen peroxide in the liquid phase to produce propylene oxide in a series of separate reaction zones each containing a packed bed of solid catalyst, wherein a reaction liquid comprised of propylene, hydrogen peroxide and propylene oxide as well as a vapor purge stream is passed through the bed of the solid catalyst at reaction conditions in each of the reaction zones, the resulting mixture is separated in each zone into a vapor stream which passes to the next reaction zone and a reaction liquid stream, the reaction liquid stream from each zone is removed and separately cooled to remove exothermic heat of reaction generated in the zone from which the liquid is removed, 60-90% of the cooled liquid is recycled to the zone from which it was removed and 10-40% of the cooled liquid is passed to the next in the series of reaction zones.
2. A process as claimed in Claim 1 characterised in that a propylene vapor stream is passed through the series of reaction zones to purge oxygen generated therein.
3. A process as claimed in Claim 1 or Claim 2 characterised in that a portion of the net hydrogen peroxide feed is fed to each reaction zone.
4. A process as claimed in any one of Claims 1 to 3 characterised in that a diluent liquid is fed to the first of the series of reaction zones.

5. A process as claimed in Claim 4 characterised in that the diluent liquid is isopropanol.
6. A process as claimed in Claim 4 characterised in that the diluent liquid is a mixture of isopropanol and methanol.
7. A catalytic converter comprised of a series of separate zones each containing a packed bed of solid catalyst, means of introducing reaction liquid into each zone and passing the liquid through the bed of solid catalyst contained therein at exothermic reaction conditions, means for removing reaction liquid from each zone, means for cooling the removed reaction liquid from each zone and recycling the main portion of the cooled liquid to the zone from which it was removed, means for passing a minor portion of the cooled liquid to the next succeeding zone, and means for withdrawing liquid product from the last of the said separate zones.

FIG-1

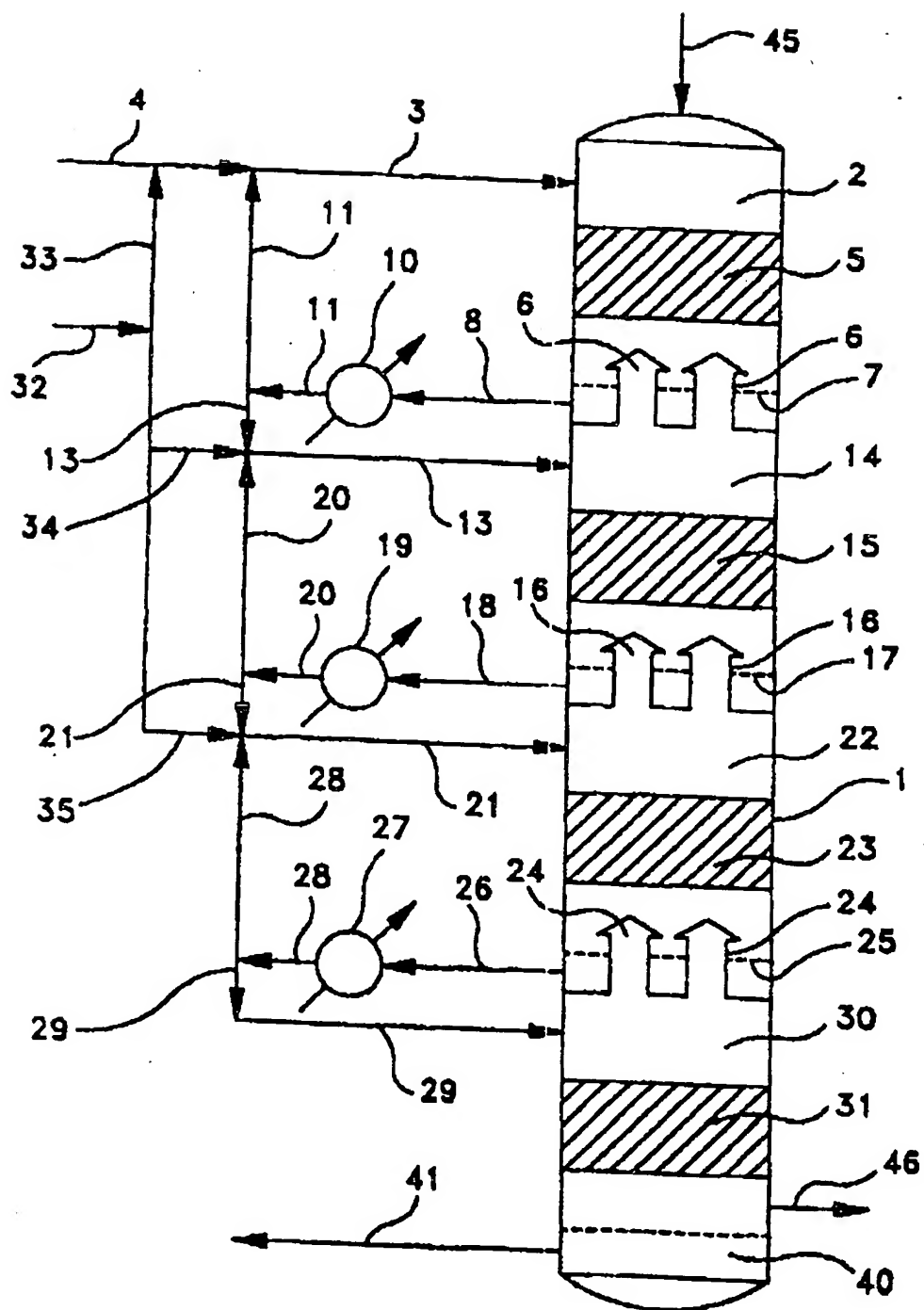


FIG-2

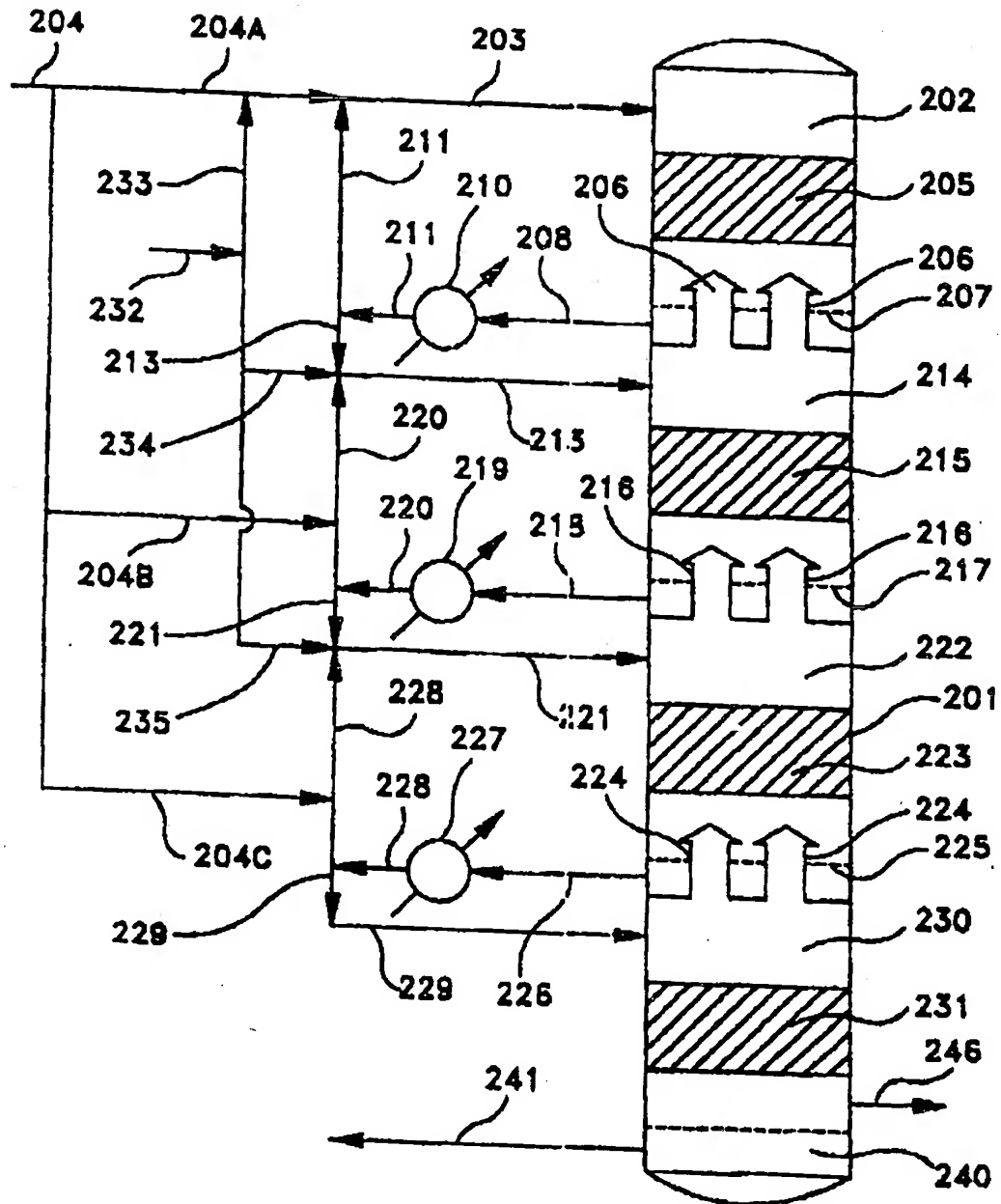
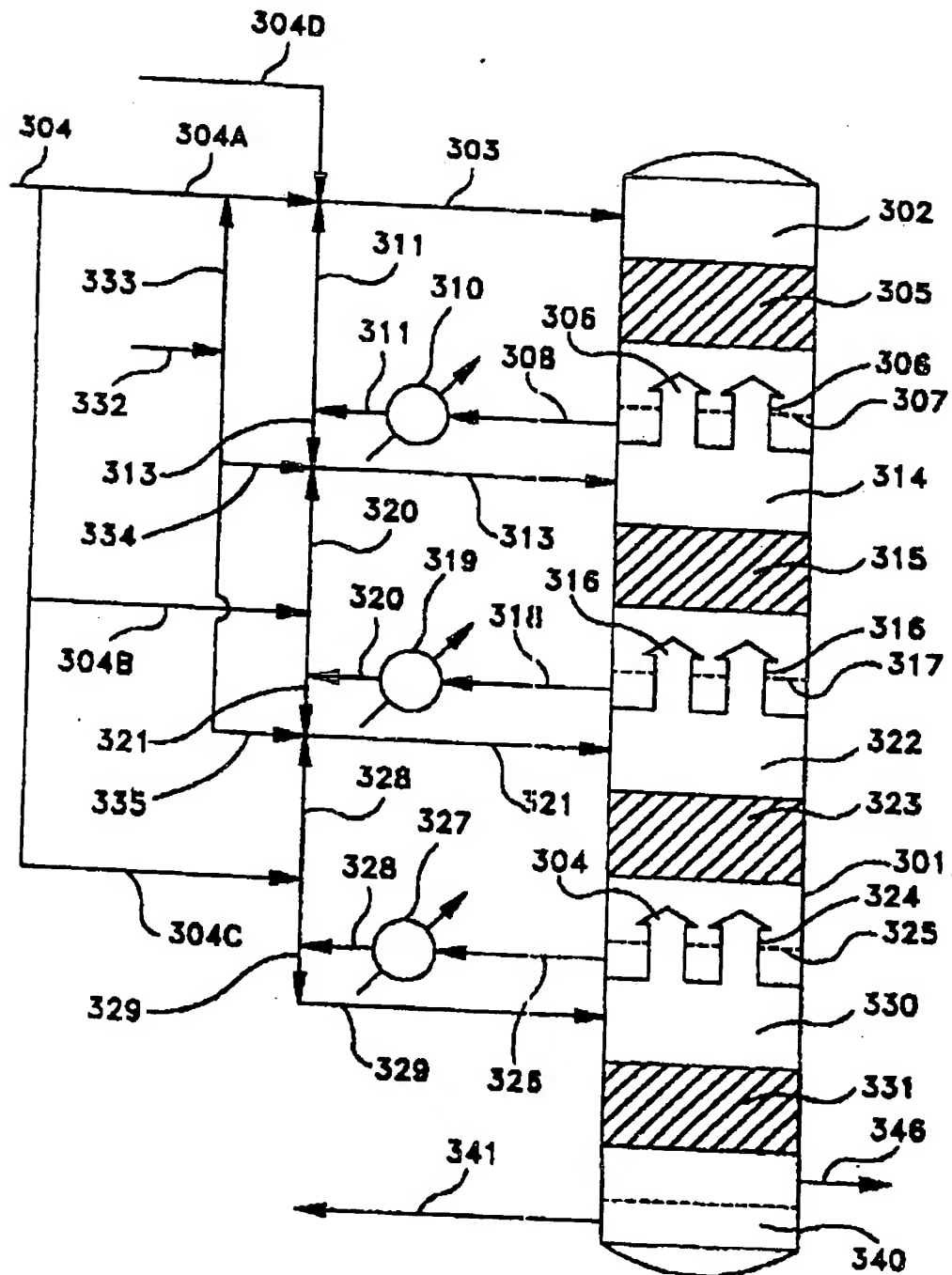


FIG-3



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 94 30 9380

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	LU-A-54 772 (NAPHTACHEMIE) * the whole document *	1, 5, 6	B01J8/04 C07D301/12
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 384 (C-629) 24 August 1989 & JP-A-01 132 573 (MITSUI TOATSU CHEM. INC.) 25 May 1989 * abstract *	1	
A	US-A-3 976 713 (SUN OIL COMPANY OF PENNSYLVANIA) * the whole document *	1, 7	
A	DE-A-22 05 057 (ESSO RESEARCH AND ENGINEERING CO.) * the whole document *	7	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B01J C07D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28 March 1995	Examiner Stevnsborg, N
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 503 (03.92) (Prelim)